

## **PATTERN FORMATION METHOD**

### **BACKGROUND OF THE INVENTION**

The present invention relates to a pattern formation method for use in fabrication  
5 process and the like for semiconductor devices.

In accordance with the increased degree of integration of semiconductor  
integrated circuits and downsizing of semiconductor devices, there are increasing demands  
for further rapid development of lithography technique. Currently, pattern formation is  
carried out through photolithography using exposing light of a mercury lamp, KrF excimer  
10 laser, ArF excimer laser or the like, and use of F<sub>2</sub> laser lasing at a shorter wavelength is  
being examined. However, since there remain a large number of problems in exposure  
systems and resist materials, photolithography using exposing light of a shorter wavelength  
has not been put to practical use.

In these circumstances, immersion lithography has been recently proposed for  
15 realizing further refinement of patterns by using conventional exposing light (M. Switkes  
and M. Rothschild, "Immersion lithography at 157 nm", J. Vac. Sci. Technol., B19, 2353  
(2001)).

In the immersion lithography, a region in an exposure system sandwiched between  
a projection lens and a resist film formed on a wafer is filled with a solution having a  
20 refractive index  $n$ , and therefore, the NA (numerical aperture) of the exposure system has a  
value  $n \cdot NA$ . As a result, the resolution of the resist film can be improved.

Now, a conventional pattern formation method using the immersion lithography  
will be described with reference to FIGS. 7A through 7D.

First, a positive chemically amplified resist material having the following  
25 composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.06 g

5 Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 7A, the aforementioned chemically amplified resist material is applied on a substrate 1 so as to form a resist film 2 with a thickness of 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 7B, while supplying water 3 onto the resist film 2, pattern exposure is carried out by irradiating the resist film 2 with exposing light 4 of ArF excimer  
10 laser with NA of 0.65 through a mask 5. Although a projection lens for condensing the exposing light 4 having passed through the mask 5 on the surface of the resist film 2 is not shown in FIG. 7B, a region sandwiched between the projection lens and the resist film 2 is filled with the water 3. Thus, an exposed portion 2a of the resist film 2 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while  
15 an unexposed portion 2b of the resist film 2 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 7C, the resist film 2 is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline  
20 developer). In this manner, a resist pattern 6 made of the unexposed portion 2b of the resist film 2 and having a line width of 0.09  $\mu\text{m}$  can be obtained as shown in FIG. 7D.

As shown in FIG. 7D, however, the resist pattern 6 formed by the conventional pattern formation method is in a defective shape.

Although the positive chemically amplified resist material is used in the above-  
25 described conventional method, also when a negative chemically amplified resist material

is used instead, the resultant resist pattern is in a defective shape.

When a resist pattern in such a defective shape is used for etching a target film, the resultant pattern is also in a defective shape, which disadvantageously lowers the productivity and the yield in the fabrication process for semiconductor devices.

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## SUMMARY OF THE INVENTION

In consideration of the aforementioned conventional problem, an object of the invention is forming a resist pattern in a good shape by the immersion lithography.

In order to achieve the object, the present inventors have examined the cause of  
10 the defective shape of the resist pattern formed by the conventional immersion lithography, resulting in finding the following: In the pattern exposure performed with the water supplied on the resist film, the water present on the resist film is evaporated, and therefore, a space, namely, a portion where there is no water, is formed in an upper portion of the region sandwiched between the projection lens and the resist film. This space causes a  
15 phenomenon that the value of the NA of the exposure system is shifted from a predetermined value or varied, resulting in causing the defective shape of the resist pattern.

The present invention was devised on the basis of this finding. According to the invention, a hygroscopic compound or a rare earth compound is supplied onto the surface of a resist film, so that the hygroscopic compound or the rare earth compound can make  
20 atmospheric vapor be incorporated into the surface of the resist film, and the invention is specifically practiced as follows:

The first pattern formation method of this invention includes the steps of forming a resist film made from a resist material including a hygroscopic compound; performing pattern exposure by selectively irradiating the resist film with exposing light while  
25 supplying water onto the resist film; and forming a resist pattern by developing the resist

film after the pattern exposure.

According to the first pattern formation method, atmospheric vapor is adhered onto the surface of the resist film owing to the function of the hygroscopic compound. The vapor adhered onto the surface of the resist film is incorporated into and integrated  
5 with the water filled between a projection lens and the resist film due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water filled between the projection lens and the resist film is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air. Therefore, no space is formed in an upper portion of a region between the  
10 projection lens and the resist film and hence the value of the NA of an exposure system can be stabilized, resulting in forming the resist pattern in a good shape.

The second pattern formation method of this invention includes the steps of performing pattern exposure by selectively irradiating a resist film with exposing light while supplying, onto the resist film, water including a hygroscopic compound; and  
15 forming a resist pattern by developing the resist film after the pattern exposure.

According to the second pattern formation method, atmospheric vapor is adhered onto the surface of the resist film owing to the function of the hygroscopic compound. The vapor adhered onto the surface of the resist film is incorporated into and integrated with the water filled between a projection lens and the resist film due to the surface tension  
20 of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water filled between the projection lens and the resist film is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air. Therefore, no space is formed in an upper portion of a region between the projection lens and the resist film and hence the value of the NA of an exposure system can  
25 be stabilized, resulting in forming the resist pattern in a good shape.

In the first or second pattern formation method, the hygroscopic compound can be ethylene glycol, polyethylene glycol, glycerin or *N*-methyl-2-pyrrolidone.

The third pattern formation method of this invention includes the steps of forming a resist film made from a resist material including a rare earth compound; performing  
5 pattern exposure by selectively irradiating the resist film with exposing light while supplying water onto the resist film; and forming a resist pattern by developing the resist film after the pattern exposure.

According to the third pattern formation method, atmospheric vapor is adhered onto the surface of the resist film owing to the function of the rare earth compound. The  
10 vapor adhered onto the surface of the resist film is incorporated into and integrated with the water filled between a projection lens and the resist film due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water filled between the projection lens and the resist film is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated  
15 from the air. Therefore, no space is formed in an upper portion of a region between the projection lens and the resist film and hence the value of the NA of an exposure system can be stabilized, resulting in forming the resist pattern in a good shape.

The fourth pattern formation method of this invention includes the steps of supplying a solution including a rare earth compound onto a resist film; performing pattern  
20 exposure by selectively irradiating the resist film with exposing light while supplying water onto the resist film onto which the solution has been supplied; and forming a resist pattern by developing the resist film after the pattern exposure.

According to the fourth pattern formation method, since the rare earth compound is present on the surface of the resist film, atmospheric vapor is adhered onto the surface of  
25 the resist film owing to the function of the rare earth compound. The vapor adhered onto

the surface of the resist film is incorporated into and integrated with the water filled between a projection lens and the resist film due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water filled between the projection lens and the resist film is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air. Therefore, no space is formed in an upper portion of a region between the projection lens and the resist film and hence the value of the NA of an exposure system can be stabilized, resulting in forming the resist pattern in a good shape.

In the fourth pattern formation method, the solution can be supplied by a paddle method, a dip method or a spray method.

The fifth pattern formation method of this invention includes the steps of forming a film including a rare earth compound on a resist film; performing pattern exposure by selectively irradiating the resist film with exposing light while supplying water onto the film; and forming a resist pattern by developing the resist film after the pattern exposure.

According to the fifth pattern formation method, atmospheric vapor is adhered onto the surface of the film owing to the function of the rare earth compound. The vapor adhered onto the surface of the film formed on the resist film is incorporated into and integrated with the water filled between a projection lens and the film formed on the resist film due to the surface tension of the water. Accordingly, even when the water filled between the projection lens and the film formed on the resist film is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air. Therefore, no space is formed in an upper portion of a region between the projection lens and the film formed on the resist film and hence the value of the NA of an exposure system can be stabilized, resulting in forming the resist pattern in a good shape.

In the fifth pattern formation method, the film including a rare earth compound

can be a nonaqueous film.

In this case, the nonaqueous film can be an olefin film, and the olefin film can be a polyethylene film, a polypropylene film or a film of a copolymer of ethylene and propylene.

5           In any of the third through fifth pattern formation methods, the rare earth compound can be an oxide, a chloride, a sulfate, a nitrate, a hydroxide, an acetate or an octylate.

          In any of the third through fifth pattern formation methods, the rare earth compound can be yttrium oxide, neodymium oxide, cerium oxide, lanthanum oxide or  
10 scandium oxide.

          In any of the third through fifth pattern formation methods, the rare earth compound can be cerium chloride.

          In any of the third through fifth pattern formation methods, the rare earth compound can be ceric sulfate or ammonium ceric sulfate.

15           In any of the third through fifth pattern formation methods, the rare earth compound can be cerium nitrate, ammonium cerium nitrate or lanthanum nitrate.

          In any of the third through fifth pattern formation methods, the rare earth compound can be cerium hydroxide.

          In any of the third through fifth pattern formation methods, the rare earth  
20 compound can be cerium acetate.

          In any of the third through fifth pattern formation methods, the rare earth compound can be cerium octylate.

          In any of the first through fifth pattern formation methods, the exposing light can be KrF excimer laser or ArF excimer laser.

25                           **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGS. 1A, 1B, 1C and 1D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 1 of the invention;

FIGS. 2A, 2B, 2C and 2D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 2 of the invention;

5        FIGS. 3A, 3B, 3C and 3D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 3 of the invention;

FIGS. 4A, 4B, 4C and 4D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 4 of the invention;

10       FIGS. 5A, 5B, 5C and 5D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 5 of the invention;

FIGS. 6A, 6B, 6C and 6D are cross-sectional views for showing procedures in a pattern formation method according to Embodiment 6 of the invention; and

FIGS. 7A, 7B, 7C and 7D are cross-sectional views for showing procedures in a conventional pattern formation method.

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## **DETAILED DESCRIPTION OF THE INVENTION**

### **EMBODIMENT 1**

A pattern formation method according to Embodiment 1 of the invention will now be described with reference to FIGS. 1A through 1D.

20        First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%)    ...    2 g

25        Acid generator: triphenylsulfonium nonaflate    ...    0.06 g



Hygroscopic compound: ethylene glycol ... 0.08 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 1A, the aforementioned chemically amplified resist material is applied on a substrate 101 so as to form a resist film 102 with a thickness of  
5 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 1B, with a region between the resist film 102 and a projection lens 106 filled with water 103 (having a refractive index  $n$  of 1.44), pattern exposure is carried out by irradiating the resist film 102 with exposing light 104 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 102a  
10 of the resist film 102 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 102b of the resist film 102 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 1C, the resist film 102 is baked with  
15 a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 105 made of the unexposed portion 102b of the resist film 102 and having a line width of 0.09  $\mu\text{m}$  can be formed in a good rectangular shape as shown in FIG. 1D.

20 In Embodiment 1, atmospheric vapor is adhered onto the surface of the resist film 102 owing to the function of the hygroscopic compound, and the vapor adhered onto the surface of the resist film 102 is incorporated into and integrated with the water 103 filled between the projection lens 106 and the resist film 102 due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even  
25 when the water 103 filled between the projection lens 106 and the resist film 102 is

evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air. Therefore, no space is formed in an upper portion of the region between the projection lens 106 and the resist film 102, resulting in forming the resist pattern 105 in a good shape.

## 5 EMBODIMENT 2

A pattern formation method according to Embodiment 2 of the invention will now be described with reference to FIGS. 2A through 2D.

First, a negative chemically amplified resist material having the following composition is prepared:

10       Base polymer: poly((norbornene-5-methylenecarboxylic acid) – (maleic anhydride)) (wherein norbornene-5-methylenecarboxylic acid : maleic anhydride = 50 mol% : 50 mol%)       ...       2 g

          Crosslinking agent: 1,3,5-*N*-(trihydroxymethyl)melamine       ...       0.7 g

          Acid generator: triphenylsulfonium nonaflate       ...       0.06 g

15       Hygroscopic compound: polyethylene glycol       ...       0.06 g

          Solvent: propylene glycol monomethyl ether acetate       ...       20 g

Next, as shown in FIG. 2A, the aforementioned chemically amplified resist material is applied on a substrate 201 so as to form a resist film 202 with a thickness of 0.35  $\mu\text{m}$ .

20       Then, as shown in FIG. 2B, with a region between the resist film 202 and a projection lens 206 filled with water 203, pattern exposure is carried out by irradiating the resist film 202 with exposing light 204 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 202a of the resist film 202 becomes insoluble in an alkaline developer due to the function of the crosslinking agent because an acid is  
25       generated from the acid generator therein while an unexposed portion 202b of the resist

film 202 remains soluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 2C, the resist film 202 is baked with a hot plate at a temperature of 120°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 205 made of the exposed portion 202a of the resist film 202 and having a line width of 0.09 μm can be formed in a good rectangular shape as shown in FIG. 2D.

In Embodiment 2, atmospheric vapor is adhered onto the surface of the resist film 202 owing to the function of the hygroscopic compound, and the vapor adhered onto the surface of the resist film 202 is incorporated into and integrated with the water 203 filled between the projection lens 206 and the resist film 202 due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water 203 filled between the projection lens 206 and the resist film 202 is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air, resulting in forming the resist pattern 205 in a good shape.

### EMBODIMENT 3

A pattern formation method according to Embodiment 3 of the invention will now be described with reference to FIGS. 3A through 3D.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 3A, the aforementioned chemically amplified resist material is applied on a substrate 301 so as to form a resist film 302 with a thickness of 0.35  $\mu\text{m}$ .

5 Then, as shown in FIG. 3B, with a region between the resist film 302 and a projection lens 306 filled with water 303 including 5 wt% of glycerin (a hygroscopic compound), pattern exposure is carried out by irradiating the resist film 302 with exposing light 304 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 302a of the resist film 302 becomes soluble in an alkaline developer  
10 because an acid is generated from the acid generator therein while an unexposed portion 302b of the resist film 302 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 3C, the resist film 302 is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is  
15 developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 305 made of the unexposed portion 302b of the resist film 302 and having a line width of 0.09  $\mu\text{m}$  can be formed in a good rectangular shape as shown in FIG. 3D.

In Embodiment 3, atmospheric vapor is adhered onto the surface of the resist film  
20 302 owing to the function of the hygroscopic compound, and the vapor adhered onto the surface of the resist film 302 is incorporated into and integrated with the water 303 filled between the projection lens 306 and the resist film 302 due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water 303 filled between the projection lens 306 and the resist film 302 is  
25 evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor

incorporated from the air, resulting in forming the resist pattern 305 in a good shape.

In each of Embodiments 1 through 3, ethylene glycol, polyethylene glycol, glycerin, *N*-methyl-2-pyrrolidone or the like can be appropriately used as the hygroscopic compound.

5 Also, the amount of the hygroscopic compound to be included in the resist film or the water can be approximately several wt%, or may be larger or smaller than this.

#### EMBODIMENT 4

A pattern formation method according to Embodiment 4 of the invention will now be described with reference to FIGS. 4A through 4D.

10 First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

15 Acid generator: triphenylsulfonium nonaflate ... 0.06 g

Rare earth compound: yttrium oxide ... 0.07 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 4A, the aforementioned chemically amplified resist material is applied on a substrate 401 so as to form a resist film 402 with a thickness of  
20 0.35  $\mu\text{m}$ .

Then, as shown in FIG. 4B, with a region between the resist film 402 and a projection lens 406 filled with water 403, pattern exposure is carried out by irradiating the resist film 402 with exposing light 404 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 402a of the resist film 402 becomes soluble in  
25 an alkaline developer because an acid is generated from the acid generator therein while an

unexposed portion **402b** of the resist film **402** remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. **4C**, the resist film **402** is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern **405** made of the unexposed portion **402b** of the resist film **402** and having a line width of 0.09 μm can be formed in a good rectangular shape as shown in FIG. **4D**.

In Embodiment 4, atmospheric vapor is adhered onto the surface of the resist film **402** owing to the function of the rare earth compound, and the vapor adhered onto the surface of the resist film **402** is incorporated into and integrated with the water **403** filled between the projection lens **406** and the resist film **402** due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even when the water **403** filled between the projection lens **406** and the resist film **402** is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air, resulting in forming the resist pattern **405** in a good shape.

#### EMBODIMENT 5

A pattern formation method according to Embodiment 5 of the invention will now be described with reference to FIGS. **5A** through **5D**.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 5A, the aforementioned chemically amplified resist material is applied on a substrate 501 so as to form a resist film 502 with a thickness of 0.35  $\mu\text{m}$ . Subsequently, a solution 503 including ammonium ceric sulfate (a rare earth compound) is supplied onto the resist film 502 for, for example, 30 seconds by a dip method or the like, and thereafter, the solution 503 is removed. Thus, the rare earth compound remains on the resist film 502.

Then, as shown in FIG. 5B, with a region between the resist film 502 and a projection lens 507 filled with water 504, pattern exposure is carried out by irradiating the resist film 502 with exposing light 504 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 502a of the resist film 502 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 502b of the resist film 502 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 5C, the resist film 502 is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 506 made of the unexposed portion 502b of the resist film 502 and having a line width of 0.09  $\mu\text{m}$  can be formed in a good rectangular shape as shown in FIG. 5D.

In Embodiment 5, atmospheric vapor is adhered onto the surface of the resist film 502 owing to the function of the rare earth compound, and the vapor adhered onto the surface of the resist film 502 is incorporated into and integrated with the water 504 filled between the projection lens 507 and the resist film 502 due to the surface tension of the water and the hydrophobic property of the surface of the resist film. Accordingly, even

when the water 504 filled between the projection lens 507 and the resist film 502 is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air, resulting in forming the resist pattern 506 in a good shape.

In order to supply the solution 503 including the rare earth compound onto the resist film 502, the solution 503 may be dropped on the resist film 502 (a paddle method), the substrate having the resist film 502 thereon may be dipped in the solution 503 (the dip method), or the solution 503 may be sprayed on the resist film 502 (a spray method). The rare earth compound included in the solution 503 can be definitely supplied onto the surface of the resist film 502 by any of these methods.

#### EMBODIMENT 6

A pattern formation method according to Embodiment 6 of the invention will now be described with reference to FIGS. 6A through 6D.

First, a positive chemically amplified resist material having the following composition is prepared:

Base polymer: poly((norbornene-5-methylene-t-butylcarboxylate) – (maleic anhydride)) (wherein norbornene-5-methylene-t-butylcarboxylate : maleic anhydride = 50 mol% : 50 mol%) ... 2 g

Acid generator: triphenylsulfonium nonaflate ... 0.06 g

Solvent: propylene glycol monomethyl ether acetate ... 20 g

Next, as shown in FIG. 6A, the aforementioned chemically amplified resist material is applied on a substrate 601 so as to form a resist film 602 with a thickness of 0.35  $\mu\text{m}$ . Subsequently, a nonaqueous film 603 (with a thickness of 0.07  $\mu\text{m}$ ) made of a polymethyl methacrylate film including 7 wt% of neodymium oxide (a rare earth compound) is formed on the resist film 602.

Then, as shown in FIG. 6B, with a region between the nonaqueous film 603 and a



projection lens 607 filled with water 604, pattern exposure is carried out by irradiating the nonaqueous film 603 and the resist film 602 with exposing light 605 of ArF excimer laser with NA of 0.65 through a mask not shown. Thus, an exposed portion 602a of the resist film 602 becomes soluble in an alkaline developer because an acid is generated from the acid generator therein while an unexposed portion 602b of the resist film 602 remains insoluble in an alkaline developer because no acid is generated from the acid generator therein.

After the pattern exposure, as shown in FIG. 6C, the resist film 602 is baked with a hot plate at a temperature of 110°C for 60 seconds, and the resultant resist film is developed with a 2.38 wt% tetramethylammonium hydroxide developer (alkaline developer). In this manner, a resist pattern 606 made of the unexposed portion 602b of the resist film 602 and having a line width of 0.09  $\mu\text{m}$  can be formed in a good rectangular shape as shown in FIG. 6D.

In Embodiment 6, atmospheric vapor is adhered onto the surface of the nonaqueous film 603 owing to the function of the rare earth compound, and the vapor adhered onto the surface of the nonaqueous film 603 is incorporated into and integrated with the water 604 filled between the projection lens 607 and the nonaqueous film 603 due to the surface tension of the water and the hydrophobic property of the surface of the nonaqueous film. Accordingly, even when the water 604 filled between the projection lens 607 and the nonaqueous film 603 is evaporated and reduced in the quantity, the reduced quantity can be covered by the vapor incorporated from the air, resulting in forming the resist pattern 606 in a good shape.

Although the polymethyl methacrylate film is used as the nonaqueous film 603 in Embodiment 6, the nonaqueous film 603 may be an olefin film such as a polyethylene film, a polypropylene film or a film of a copolymer of ethylene and propylene instead.

The rare earth compound used in each of Embodiments 4 through 6 may be appropriately selected from an oxide, a chloride, a sulfate, a nitrate, a hydroxide, an acetate and an octylate. The amount of the rare earth compound to be included in the resist film, the water or the nonaqueous film can be approximately several wt%, or may be larger or  
5 smaller than this.

Examples of the oxide of the rare earth compound are yttrium oxide, neodymium oxide, cerium oxide, lanthanum oxide and scandium oxide.

An example of the chloride of the rare earth compound is cerium chloride.

Examples of the sulfate of the rare earth compound are ceric sulfate and  
10 ammonium ceric sulfate.

Examples of the nitrate of the rare earth compound are cerium nitrate, ammonium cerium nitrate and lanthanum nitrate.

An example of the hydroxide of the rare earth compound is cerium hydroxide.

An example of the acetate of the rare earth compound is cerium acetate.

15 An example of the octylate of the rare earth compound is cerium octylate.

Furthermore, in each of Embodiments 1 through 6, the exposing light can be KrF excimer laser, F<sub>2</sub> laser, KrAr laser, Ar<sub>2</sub> laser or the like instead of the ArF excimer laser.

Moreover, in each of Embodiments 1 through 6, the water supplied onto the resist film may include an additive such as a surfactant if necessary.

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